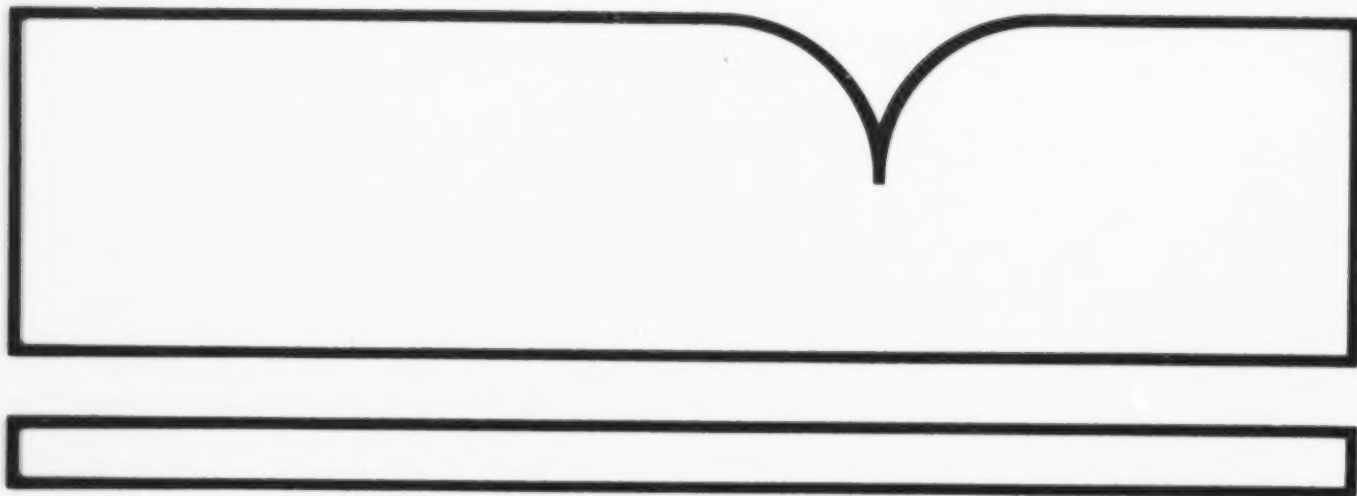


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Physical and Chemical Factors That
Influence the Anaerobic Degradation of
Methyl Parathion in Sediment Systems

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PHYSICAL AND CHEMICAL FACTORS THAT INFLUENCE THE ANAEROBIC DEGRADATION OF METHYL PARATHION IN SEDIMENT SYSTEMS

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Abstract—The kinetics of disappearance of methyl parathion (0,0 dimethyl-0-*p*-nitrophenyl phosphorothioate) were studied in anaerobic sediment samples in the laboratory as a function of methyl parathion concentration, pH and Eh. The disappearance of methyl parathion is described by first-order kinetics and amino methyl parathion (0,0-dimethyl-0-*p*-aminophenyl phosphorothioate) was identified as a reduction product. In the strongly reducing sediments, the half-lives were on the order of a few minutes. In water isolated from the sediment, no reaction could be detected over the period of a week. Also, there is no apparent correlation between the first-order disappearance rate constants and the pH of the sediment samples. In heat-sterilized sediments, the disappearance rate constants are retarded about two orders of magnitude relative to nonsterile sediments. In chemically treated sediments, first-order disappearance rate constants are comparable to those in the nonsterile system.

Keywords—Kinetics Redox Methyl parathion Sediments Pesticide

INTRODUCTION

Qualitative descriptions of oxidation-reduction (redox) reactions of organic pollutants have been reported in soils [1], sediments [2] and natural waters [3]. These studies suggest that redox transformations of organic compounds can be an important degradation pathway. No quantitative descriptions of the redox transformations, however, have been reported that permit one to assess the significance of this process in aquatic ecosystems [4].

Failure to take into account redox processes can result in an overestimation of the exposure concentrations of certain organic compounds in ecosystems when strongly oxidizing or reducing conditions exist [5]. For example, the calculated neutral and alkaline hydrolysis half-lives for methyl parathion at pH 9 and 25°C are 11 and 13 weeks, respectively [6]. The microbial degradation half-life—assuming 10^7 organisms/L—is 9 weeks (D. Paris, personal communication). In contrast, half-lives of less than 1 h have been observed for

methyl parathion under the reducing conditions (anaerobic) that are typical of soils and sediments [7].

To better define the kinetic parameters that govern the redox transformation of organic compounds, we used a model compound for which the redox reaction kinetics are known. This paper reports the preliminary findings on the kinetics of transformation of methyl parathion in selected reducing sediments in laboratory studies. The disappearance reaction kinetics in sediment-water samples were examined as a function of initial concentration of the compound over a range of Eh and pH levels, sediment concentrations, and varying microbial activities.

EXPERIMENTAL SECTION

Materials

Analytical grade methyl parathion (0,0-dimethyl-0-*p*-nitrophenyl phosphorothioate) was obtained from the Pesticides and Industrial Chemicals Repository, U.S. Environmental Protection Agency (Research Triangle Park, NC). Analyses by GLC, HPLC and GLC-MS showed no detect-

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able impurities in methyl parathion. Analytical grade isooctane and acetonitrile were purchased from Burdick and Jackson.

Measurements of pH in samples collected at the Georgia sites were made with a Corning Model 112 pH meter equipped with an Orion No. 91-62 pH probe. The probe was calibrated prior to measurement with commercially available pH buffers. Eh measurements were made using a Corning 4 portable pH TempMeter and a Markson No. 1202 combination platinum (button)/reference (silver-silver chloride) electrode. The electrode was checked against a standard ferrous-ferric solution prior to making measurements [8]. In the event the electrode gave a reading that was not within ± 5 mV of the value of the standard solution the electrode was cleaned using a 10% hydrogen chloride solution followed by a 10% hydrogen peroxide solution and then rinsed with distilled water. This procedure was repeated until the value of the reference standard (Eh = 750 mV, 25°C) was maintained.

The redox potentials of sediment samples, collected and returned to the laboratory at the Colorado School of Mines, were determined following a similar procedure only using a wax impregnated graphite electrode (WIGE).

Analyses for methyl parathion by GLC were performed on a Tracor MT-220 gas chromatograph equipped with a 1.6-m $\times$ 4.0-mm i.d. column packed with 3% SE 30 on 80 to 100 mesh Crom Q. Column, inlet and detector temperatures were 200, 170 and 250°C, respectively, with a N_2 flow rate of 30 cm³/min.

Analyses for methyl parathion, amino methyl parathion (0,0-dimethyl-0-*p*-aminophenyl phosphorothioate), *p*-nitrophenol and *p*-aminophenol were carried out with a Tracor 950 liquid chromatograph using a Tracor 970A variable wavelength detector. The following conditions were typical of those used throughout the studies: a 25-cm $\times$ 4.6-mm i.d. column containing Partisil 10, an ODS 3 column, with 80% acetonitrile-20% water as the mobile phase, a flow rate of 1.5 ml/min at 890 psi and a detector wavelength of 280 nm.

Mass spectra were obtained using a Finnigan MAT automated chromatograph/EI mass spectrum system employing a 30-m-long by 0.32-mm i.d. fused silica 1 μ m DB5, capillary column. The helium carrier gas flow volume was 75 cm³/sec at 24 psi head pressure. The column was temperature programmed from 60 to 280°C with an initial hold of 2 min and a final hold of 16 min.

The sediment-to-water ratios (ρ)—expressed as grams of sediment per grams of water—were calculated based on the dried (110°C) weight of the sediment. The sediment-to-water ratios were varied for a given sediment by either centrifuging the sample and withdrawing an aliquot of water or diluting the sediment with water from a duplicate sample. The Eh and pH of the sediments were determined again after this procedure.

Methods

Sediment samples were collected at sites in Georgia, Colorado and Oklahoma. In Georgia, sediment collection sites were three ponds—Memorial Park, Bar H and Hickory Hills (2500, 1500 and 500 m² in area, respectively)—and a slow moving, shallow stream (1-m maximum depth) with a high sediment load—Beaver Dam—near the Athens Laboratory. The sediment samples were collected as follows. A glass quart jar was submerged in the pond and filled with water overlying the sediment surface. The jar was then pushed along the sediment surface to collect the top 2 to 3 in. of material. The jar was capped under water, returned to the laboratory and stored either in the dark at 8°C or under a N_2 atmosphere at room temperature. Prior to use in kinetic studies, generally within 2 d, the sediments were filtered through a 1-mm sieve to remove debris.

In Colorado, samples were collected at three sites near the city of Golden. The first was Mines Park Pond, an artificial catchment of approximately 700 m². The samples were collected in approximately 0.7 m of water and consisted of a black, sulfurous, organic-rich muck. The second sample, a black, organic-rich muck, was collected from an approximately 80 m², cattail-filled marsh in Thornton in about 10 cm of water. The third sample was collected from Chatfield Reservoir, a water supply reservoir in the South Platte River southeast of Denver. The sample was collected in 1.3 m of water and consisted of a fine, mucaceous, black-gray, organic-rich sediment with a faint sulfurous smell. The sediment samples were collected as follows. The upper 25 cm of sediment was collected from reducing aqueous environments with a 4-in.-diameter driver sampler. Samples were immediately transferred to 1-gallon plastic containers, sealed with vinyl tape and stored at 4°C.

In Oklahoma, aquifer sediment samples were obtained by Dr. John Wilson of the Robert S. Kerr Environmental Research Laboratory in Ada. Visual inspection showed the samples to be a light to dark tan, well-sorted, fine sand containing occa-

sional root hairs. All samples were received in sealed glass containers and were stored at 4°C.

Kinetic procedures

The description below is representative of the kinetic procedures that were used throughout these studies.

The bulk sediment sample was placed in a glove box under a N₂ atmosphere. Aliquots (4 ml) were transferred (pipette) to 10-ml serum bottles that were subsequently fitted with Teflon/silicone disks and capped. The samples were equilibrated for 30 min at the desired temperature and then spiked with 50 µl of 2.0 × 10⁻⁵ M methyl parathion in distilled water followed by 1 min of mixing on a vortex shaker. The samples were then placed on a rotary shaker at 22°C. At selected time intervals, 1 ml of acetonitrile followed by 3 ml of isooctane were added to the serum bottles with a syringe to quench the reaction. The samples were then mixed (vortex shaker) for about 2 min and allowed to stand for at least 2 h before analysis of the isooctane layer by GLC. Concentrations of methyl parathion were calculated by comparing peak heights for the compound in the isooctane with those of the prepared standards. Recoveries at time zero were greater than 95% of the methyl parathion added. Pseudo first-order rate constants were calculated from the concentration-time data by least-squares analysis.

Kinetic studies were also carried out in water isolated from the sediment samples. The water was obtained by centrifuging a portion of the sediment sample in tubes under a nitrogen atmosphere. The samples were centrifuged at 2500 rpm for 10 min, transferred to a glove box under a nitrogen atmosphere where the kinetic studies were carried out as described above.

Microbial activity

Sediment samples were sterilized using two different techniques. Heat sterilization was accomplished by autoclaving the samples in serum bottles for 20 min at 110°C. In most cases, this procedure had to be repeated a total of three times on three consecutive days to assure sterilization. Chemical sterilization was accomplished by adding enough formaldehyde to give a resulting concentration of 0.1 M (based on sediment volume) of sterilant. Sediment samples containing predetermined concentrations of *m*-cresol (based on sediment volumes) were obtained by adding calculated quantities of *m*-cresol. Water samples were sterilized by filtering using 0.22-µm Nuclepore filters.

The criterion for sterility for aerobic samples, using the standard plate count, and for anaerobic samples, using the Hungate roll tube, was no bacterial growth after five days.

RESULTS AND DISCUSSION

The four sample sites near the Environmental Research Laboratory, Athens, Georgia, were selected to facilitate sampling and insure that kinetic studies could be initiated within 2 d of the time of sampling. Although it is desirable to extensively characterize the sediments based on physical and chemical criteria, in these initial studies the sediment samples were characterized only by Eh and pH. The Eh and pH of the water column and the sediment taken at sample sites at the time of sampling are shown in Table 1. In general, the pH of the water column decreased with depth by no more than 1 pH unit. Variation of Eh with increasing depth was more pronounced, decreasing with increasing depth and showing the largest decrease at the sediment surface.

Table 1. Characteristic pH and Eh ranges of sample sites near Athens, Georgia (surface water, sediment surface and 1 in. into sediment)

Sampling location	Range ^a	
	pH ^b	Eh, mV ^c (SHE)
Beaver Dam		
water column	5.52-5.82	225/378
sediment surface	5.66-5.78	77/332
top 1 in. of sediment	5.42-5.55	59/300
24 h in lab (sed)	6.54	-90
Memorial Park pond		
water column	6.81-6.97	26/127
sediment surface	7.18-7.30	124/135
top 1 in. of sediment	7.37-7.49	-127/-223
after 24 h in lab (sed)	6.10	-228
Hickory Hills pond		
water column	7.21-7.56	250/385
sediment surface	6.97-7.59	404/180
top 1 in. of sediment	7.40-7.60	316/-154
after 24 h in lab (sed)	7.05	-179
Bar II		
water column	6.10-7.09	37/-116
sediment surface	6.20-6.39	36/-117
top 1 in. of sediment	5.98-6.18	-150/-182
24 h in lab (sed)	7.32	-19

^aThe range of values, Eh and pH, obtained by making measures within a circle of approximately 1 m radius.

^bpH meter was calibrated with standard buffers ± 0.02 pH units.

^cValues were determined using a platinum button electrode. Electrode was generally equilibrated for 30 min prior to taking the readings.

Sediment samples were monitored in the laboratory for Eh and pH during the course of the experiments. In general, Eh did not vary more than ± 15 mV for the samples stored under a nitrogen atmosphere at room temperature over a period of two weeks. The pH did not vary more than 0.2 pH units. Within experimental error, autoclaving the sediment samples at 110°C for 20 min did not change the Eh or pH of the sediment.

Eh measurements were made using two different types of electrodes. In sediment samples from Georgia, a platinum electrode was used and in samples from Colorado and Oklahoma a wax impregnated graphite electrode (WIGE) was used. No attempt was made to compare the magnitudes of the measured Ehs; there is no apparent correlation, however, with the disappearance rate constants. For a detailed comparison of the response behavior of these electrodes, Macalady et al. [9], in a related kinetic study, has evaluated the two electrodes for reproducibility, stability and measured potentials.

In general, the disappearance of methyl parathion in these sediment systems is satisfactorily described by the first-order kinetic expression. This statement is supported by the results of two sets of experiments. The first results show that the first-order expression is observed through at least three half-lives of reaction. A typical first-order plot is given in Figure 1 for the disappearance of methyl parathion with an initial concentration of 2×10^{-8} M in a reducing sediment at Eh 89 mV (versus SHE) and pH 6.9. The second set of results complement the first findings in that they show that the disappearance rate constant for methyl parathion was independent of the initial concentration. The average value and the standard deviation of the disappearance rate constant is $(2.8 \pm 0.5) \times 10^{-2} \text{ min}^{-1}$ for initial concentrations of 2×10^{-8} , 6×10^{-8} and 3×10^{-7} M in the same sediment sample.

It was noted early in the kinetic studies of reduction reactions that mixing, under certain conditions, could have a pronounced effect on the reaction kinetics. For experiments where the reaction vessels were shaken at least every 30 min, the first-order kinetic expression was followed through three or four half-lives. For experiments in which the reaction vessels were shaken no more than once an hour, the reaction would follow first-order kinetics for the first hour and then deviate from first-order as evidenced by a decrease in the rate of reaction. It also was observed that if the sample tubes were shaken vigorously and continuously

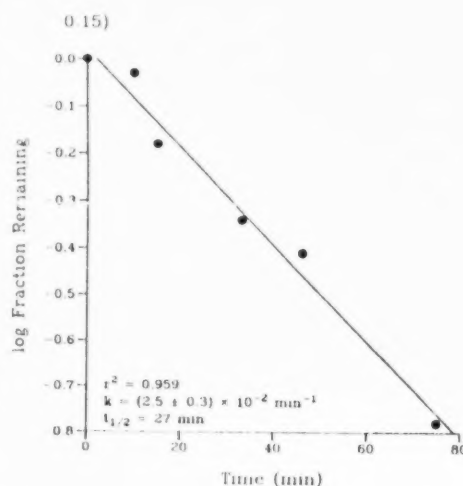


Fig. 1. First-order plot for the disappearance of methyl parathion in a reducing sediment sample (pH = 6.9, Eh = -89 mV, $\rho = 0.15$).

such as on a 360° rotating shaker, the reaction would proceed for about an hour and then slow down. An obvious color change from light gray to light brown was noted. Within experimental error, there was no change in Eh or pH of the bulk sediment.

Therefore, throughout these studies, the reaction vessels were agitated slowly on a mechanical shaker either continuously or at 30-min intervals. Under these conditions, first-order kinetics were observed and reproducible results were obtained. In general, rate constants for a given batch of sediment were reproducible with a relative standard deviation of $\pm 20\%$.

On the other hand, it was shown that the solid phase is required to carry out the transformation. In the isolated water phase, separated from the sediment by centrifuging and decanting under a nitrogen atmosphere, there was greatly reduced if any reduction at all of methyl parathion.

The only product observed in the kinetic studies was shown to be amino methyl parathion (Fig. 2). Product studies were carried out at elevated concentrations of methyl parathion in which both the disappearance of methyl parathion and the appearance of amino methyl parathion were monitored by an HPLC method using direct aqueous injections. The results of one such study are shown in Figure 3. Amino methyl parathion as a product was confirmed by GC-MS. Analysis of the solvent

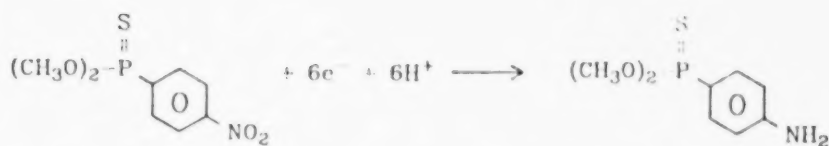


Fig. 2. The half-cell equation showing the reduction of methyl parathion to amino methyl parathion.

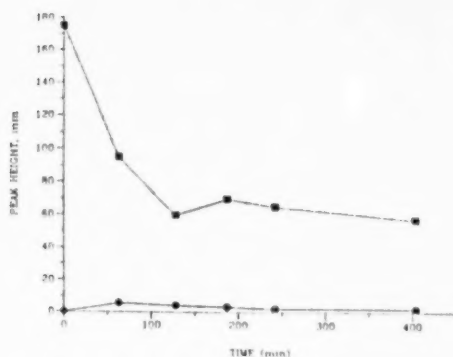


Fig. 3. A set of data showing the disappearance of methyl parathion and the appearance of amino methyl parathion with time in a reducing sediment sample.

extract (methylene chloride) of a sediment sample after one disappearance half-life showed the presence of a compound for which the mass spectra was consistent with that predicted for amino methyl parathion. Because an authentic sample of amino methyl parathion was not available and because the extinction coefficient was unknown, the rate constant of formation of the product was not calculated, and so it could not be compared with the rate of disappearance of the parent compound in these experiments.

Several studies have addressed the relationship between the Eh of a sediment and its reducing ability [4,10]. To evaluate Eh as a predictor of nitro reduction, disappearance rate constants in Beaver Dam sediment samples were compared with the measured Eh at the time of the experiment. The sediment samples were collected at the same site at various time intervals. The Eh of the sediments varied at this sample site but the reason for this variation is unknown. The data are plotted in Figure 4 along with linear regression analysis data. The results are encouraging based on the fact that the model accounts for about 99% of the variance of the data. Unfortunately, it is difficult

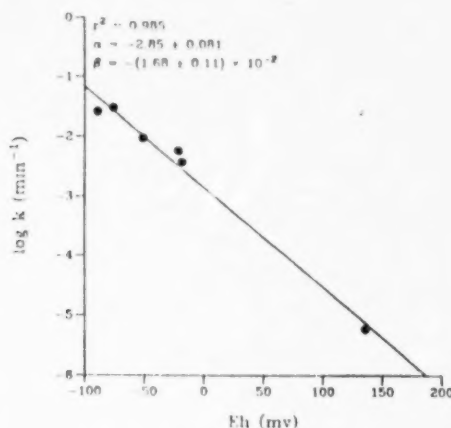


Fig. 4. Effect of Eh on the disappearance rate constant for methyl parathion in sediment water samples collected from the same sample site.

to test the model over a large range of Eh because there is not a meaningful way to vary Eh of the sediment in the laboratory and maintain the redox integrity of the sample.

To further test this proposed relationship, disappearance rate constants were obtained for the reduction of methyl parathion in sediment samples collected from the three additional Georgia sample sites (Table 1). The results, summarized as disappearance rate constants, are given in Table 2. From these results, it appears that the disappearance rate constants do not correlate with the measured Ehs of the sediments.

Additional evidence for the lack of such a correlation was obtained with anaerobic sediment samples collected from other geographical locations. Sediment samples obtained from ponds near Golden, Colorado, and Ada, Oklahoma, gave results similar to those reported for the different sediment samples from Athens, Georgia. The results summarized in Table 3 show there is no apparent correlation between Eh and the disappearance rate constants. Furthermore, there is not

Table 2. Disappearance rate constants for methyl parathion in sediment samples from the four sampling locations near Athens, Georgia

Sediment	Rate constant ^a	ρ^b	1 h ^c	pH
	10 ³ , min ⁻¹			
Beaver Dam	3.5 ± 0.6	0.15	14	6.7
Memorial Park	2.9 ± 1.2	0.20	11	6.5
Hickory Hills	2.8 ± 2.4	0.17	-47	6.9
Bar H	0.74 ± 0.25	0.14	-26	6.2

^aMean and average deviation.

^b ρ is the sediment to water ratio in g sediment/g water.

^cDetermined using a platinum button electrode.

an apparent correlation among pH, sediment concentration or organic carbon.

Several observations are apparent from this data (Table 3). The first is the large difference in the magnitude of the rate constants obtained at the same sample sites. The second is the very short half-lives (less than a minute) observed for some sediment samples. The third is that although the half-life was somewhat longer in the aquifer sample, the reaction did occur. The important thing to note, however, is that in all the sediment samples the nitro group was reduced.

Although the first study suggests that Eh may

reflect reactivity in a given sediment sample, samples from different sites do not show a good correlation. Eh is a thermodynamic parameter that has often been considered to be an indicator of redox activity of soils, sediments and natural waters. There is, however, no theoretical basis by which one can relate the redox potential as measured by a WEIC or platinum electrode to the reduction of a nitro group. Although Eh may not be proportional to the activity of the reducing agent, in a qualitative or maybe even semiquantitative way, it appears to be an indicator of the ability of the sediment to carry out reduction of the nitro group to an amino group. It is generally observed in these studies that the reduction does not occur for sediments with Ehs above 100 mV.

The effect of pH on the reaction kinetics was investigated in a limited study. In these experiments, sediment samples were titrated with acid or base to adjust the bulk pH of the samples over the range of about pH 2 to pH 10. Each sample was spiked with methyl parathion and the reaction was allowed to proceed for 1 h at which time the reaction was quenched and the percentage of methyl parathion remaining was determined. A plot of the data in Figure 5 shows that there is not a pronounced effect of pH on the reaction although the reaction does appear to be favored at alkaline

Table 3. Selected characteristics and kinetic data for methyl parathion reduction in sediment samples collected near Golden, Colorado, and Ada, Oklahoma

Sample	Eh ^a (mV vs SHE) ± 10 mV	pH	ρ^b	% loss on ignition	$t_{1/2}$ (min)	k_{obs} (min ⁻¹)	Comments
Mines Park Pond							
MP5-A	-115	—	0.09	22	22	0.032	
MP5-B	-100	7	0.09	22	36	0.019	
MP5-C ^c	-35	7	0.09	26	>3700	<2 × 10 ⁻⁴	No degradation observed for 500 min ^d
MP5-D ^c	-40	6	0.18	16	>1850	<4 × 10 ⁻⁴	No degradation observed for 250 min ^d
MP6-A	-150	6.6	0.14	7	<1	>0.69	
MP6-B	-75	7.4	0.11	8	<1	>0.69	
MP6-C	-275	8.7	0.09	9	<1	>0.69	
MP6-D	-150	8.7	0.06	13	0.75	0.92	Observed for one half life only
Chatfield Reservoir							
CH5	-195	7.4	0.10	13	16	0.042	
Aquifer							
A01	-150	8.6	0.82	1.6	596	0.012	pH rose during experi- ment from 8.6-8.9

^aMeasured using a vanadium electrode.

^aMeasured using a wax impregnated graphite electrode.

^b ρ is g sediment/g water.

^cHeat sterilized samples.

^dWithin experimental error of $\pm 10^3$ s.

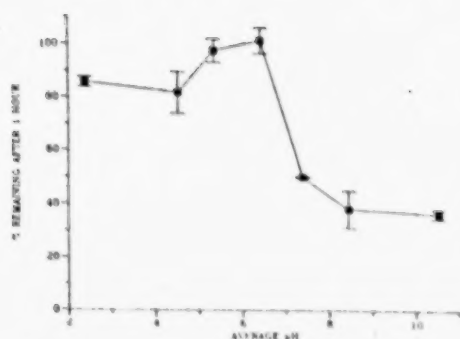


Fig. 5. Plot of the percent methyl parathion remaining in a given sediment sample after 1 h at various pHs. The sediment sample was divided into seven subsamples and the pH adjusted by the addition of acid or base prior to spiking with methyl parathion.

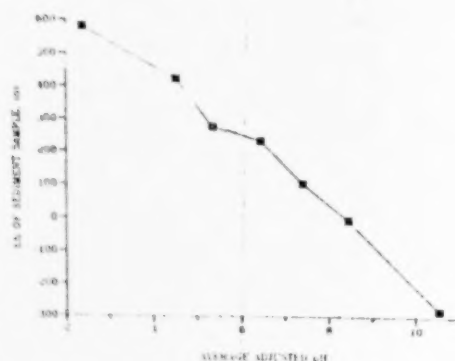


Fig. 6. An example of the response of Eh as a result of changing pH. The plotted pHs were obtained by titrating the sediment sample with acid and base.

pHs. Based on the neutral ($5.4 \times 10^{-6} \text{ min}^{-1}$) and alkaline ($0.59 \text{ M}^{-1} \text{ min}^{-1}$) hydrolysis rate constants for methyl parathion [6] and studies on organophosphorothioate esters in sediments [11], abiotic hydrolysis is negligible under these reaction conditions for this experiment, i.e., at pH 2, $t_{1/2} = 89$ days and pH 10 $t_{1/2} = 8$ days.

Figure 6 is a plot of the Eh measured at each pH investigated in the experiment. It is seen that as the pH varied from pH 2.38 to 10.54, the Eh varied from 581 to -280 mV. In contrast, the percent reaction as determined in the above experiment varied no more than a factor of 2 to 3. Thus these results support the previous observations that Eh does not relate quantitatively to the disappearance rate constant for the reduction of methyl parathion.

Based on the short half-lives and adherence to the first-order rate expression, it was postulated that the reactions were abiotic. To further support this, kinetic studies were carried out on sediment samples that were either heat sterilized, chemically sterilized with formaldehyde, or treated with *m*-cresol, a reductive dehydrogenase enzyme inhibitor. In heat sterilized experiments the rate constants, relative to the raw sediment, were decreased by about a factor of 50 to 100. For the formaldehyde experiments, the rate constants also were decreased by about a factor of 50. In the *m*-cresol experiments, the rate constants were decreased by only a factor of 2. Samples spiked with *m*-cresol at 1, 5 and 10 μM showed no microbial growth using both aerobic (standard plate count) and anaerobic (Hungate roll tube) enumeration tech-

niques. These experiments, although not conclusive, suggest an abiotic and an enzymatic contribution. Although these findings are consistent with more detailed studies by Sanders and Wolfe [12], additional work is needed to quantitate the contribution of the biotic and abiotic pathways.

CONCLUSION

These studies demonstrate the feasibility of carrying out kinetic studies in anaerobic sediment samples. They also indicate the usefulness of kinetic techniques to elucidate the activity and order of reactants in redox reactions. It is apparent that additional variables other than Eh and pH are playing roles in this nitro reductive process. One of several factors that needs to be defined before accurate models can be developed is the effect of sediment sorption on the reaction kinetics and these experiments are in progress.

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